### BAKER BOTTS L.L.P. 30 ROCKEFELLER PLAZA NEW YORK, NEW YORK 10112-0228 TO ALL WHOM IT MAY CONCERN:

Be it known that I, YANDAPALLI DURGA PRASAD, a citizen of India, having a residence at First Road, Bhaskarapuram 21-339-5, Machilipatnam, Krishna District, 521 001, Andhra Pradesh, India, have invented an improvement in

## AGROPOLYMER MATERIAL FOR USE IN WATER PURIFICATION AND A METHOD OF PRODUCING THE SAME

of which the following is a

#### **SPECIFICATION**

[0001] This application is a continuation of International Publication Number WO 00/50167, published in English on August 31, 2000, filed as International Application Number PCT/IN00/00015 on February 24, 2000, which claims priority from Indian Patent Application Number 222/MAS/99 filed February 24, 1999 and Indian Patent Application Number 223/MAS/99 filed February 24, 1999.

#### FIELD OF THE INVENTION

[0002] The present invention generally relates to the field of agricultural biotechnology. In particular, this invention pertains to a novel agropolymer and a method of manufacturing the agropolymer from plant parts such as seed coats, hulls, husks or seed covers of plants including agricultural crops. The agropolymers disclosed herein have extensive industrial applications and may be useful in purifying water or aqueous solutions polluted or contaminated by metal or ions.

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#### **BACKGROUND OF THE INVENTION**

[0003] Several biologically originating metal sequestration agents are known in the art. Examples of such agents include tannins, humic acid, whole cell biomass, chitin and chitin derivatives, metallothioneins, microbial polysaccharides, melannins, polyphenolic biopigments, bacterial cell wall polymers, microbially produced chelating agents (siderophores), and the like. However, the above materials may be costly and often are not available in sufficient quantities. Specifically, the substances known in the art have not been successfully produced on large scale for industrial use because of the low availability of raw materials and the high production costs.

[0004] Furthermore, the substances known in the art may be less effective than the agropolymer disclosed herein. Thus, the present invention is aimed at producing agropolymers, which are effective in sequestering metals and ions from polluted or contaminated aqueous solutions and which derive from inexpensive, widely available plant materials, preferably raw agricultural materials, such as seed coats, hulls, husks, or seed covers of agricultural crops.

#### **SUMMARY OF THE INVENTION**

[0005] An objective of the present invention is to provide novel agropolymers that originate from plant materials, such as the seed coats, husks, hulls, or seed covers of agricultural crops. Agricultural crops which may be employed in forming the agropolymers of the present invention include *Oryza sativa*, *Panicum miliaceum*, *Setaria italica*, *Cajanus cajan*, *Vigna mungo*, *Vigna radiata*, *Triticum sp.*, *Ricinus communis*, *Helianthus annus*, *Gossypium sp.*, and *Arachis sp.* 

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[0006] Another object of the present invention is to provide an agropolymer material that originates biologically and that is non-toxic, biodegradable, inexpensive, widely available, and effective. Such an agropolymer may be derived from agricultural sources.

[0007] Still another objective of the present invention is to develop a method for producing the agropolymer materials disclosed herein and a method of using the agropolymers in industrial applications such as sequestering or removing metals or ions from water or aqueous solutions. Such industrial applications would enable the agropolymer to aid in improving water pollution control and reducing overall environmental pollution.

[0008] Yet another object of the present invention is to provide a method of removal of heavy metals and ions from aqueous solutions using the agropolymers disclosed herein.

[0009] Still another objective of the present invention is creating a method of water purification which uses natural, biological agricultural resources, which are abundant in nature and thus readily available.

[0010] Therefore, a further object of the present invention is to provide a method of producing an agropolymer material comprising a carbohydrate and/or silica matrix substantially devoid of proteins, tannins, pigments and polyphenols, wherein the agropolymer material has metal binding reactive sites.

[0011] One skilled in the art will appreciate that the various embodiments disclosed herein, as well as other embodiments within the scope of the invention, will have numerous applications in the environmental, chemical, and biological fields.

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#### BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The present invention may be better understood with reference to the attached drawings described below:

[0013] FIGURES 1(A), (B), and (C): IR spectra of a raw rice husk sample.

[0014] FIGURES 2(A), (B), and (C): IR spectra of a rice husk sample treated with alkaline hydrogen peroxide.

[0015] FIGURES 3(A), (B), and (C): IR spectra of a raw rice husk sample treated with ferric chloride.

[0016] FIGURES 4(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated rice husk sample, which was subsequently treated with ferric chloride.

[0017] FIGURES 5(A), (B), and (C): IR spectra of a raw Setaria italica husk sample.

[0018] FIGURES 6(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated Setaria italica husk sample.

[0019] FIGURES 7(A), (B), and (C): IR spectra of a raw Setaria italica husk sample treated with ferric chloride.

[0020] FIGURES 8(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated Setaria italica husk sample which was subsequently treated with ferric chloride.

[0021] FIGURES 9(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated wheat husk sample.

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[0022] FIGURES 10(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated wheat husk sample which was subsequently treated with ferric chloride.

[0023] FIGURES 11(A), (B), and (C): IR spectra of a *Panicum miliaceum* husk sample.

[0024] FIGURES 12(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated *Panicum miliaceum* husk sample which was subsequently treated with ferric chloride.

[0025] FIGURES 13(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated cotton seed (*Gossypium sp.*) hull sample.

[0026] FIGURES 14(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated cotton seed (*Gossypium sp.*) hull sample which was subsequently treated with ferric chloride.

[0027] FIGURES 15(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated castor (*Ricinus communis*) seed coat sample.

[0028] FIGURES 16(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated castor (*Ricinus communis*) seed coat sample which subsequently was treated with ferric chloride.

[0029] FIGURES 17(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated sunflower (*Helianthus annus*) seed coat sample.

[0030] FIGURES 18(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated sunflower (*Helianthus annus*) seed coat sample which subsequently was treated with ferric chloride.

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[0031] FIGURES 19(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated redgram (*Cajanus cajan*) seed coat sample.

[0032] FIGURES 20(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated redgram (*Cajanus cajan*) seed coat sample which subsequently was treated with ferric chloride.

[0033] FIGURES 21(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated greengram (*Vigna radiata*) seed coat sample.

[0034] FIGURES 22(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated greengram (*Vigna radiata*) seed coat sample which subsequently was treated with ferric chloride.

[0035] FIGURES 23(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated blackgram (*Vigna mungo*) seed coat sample.

[0036] FIGURES 24(A), (B), and (C): IR spectra of an alkaline hydrogen peroxide treated blackgram (*Vigna mungo*) seed coat sample which subsequently was treated with ferric chloride.

#### **DETAILED DESCRIPTION OF THE INVENTION**

[0037] The present invention is directed to providing a novel agropolymer having metal binding sites, which are incorporated into a matrix of the agropolymer either by alkali treatment, hydrogen peroxide treatment, or a combination alkaline hydrogen peroxide treatment. More particularly, this invention relates to the use of the agropolymer disclosed herein in the purification of water or aqueous solutions polluted by metals or ions, including the purification

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of industrial ground water and drinking water. Such a purification method is possible because of the capability of the agropolymer to sequester metals and/or ions found in polluted or contaminated water or aqueous solutions.

[0038] The matrix of the agropolymer is obtained from any plant parts such as seed coats, seed covers, hulls and husks. The metal binding reactive sites (which facilitate organometallic bonds) are created by reacting the agropolymers with metals as observed under infrared (IR) spectroscopy.

[0039] The agropolymers of the present invention may be produced from plant materials (such as seed coats, seed covers, hulls, or husks) of agricultural crops, and the crops appropriate for use herein may include *Oryza sativa*, *Panicum miliaceum*, *Setaria italica*, *Cajanus cajan*, *Vigna mungo*, *Vigna radiata*, *Triticum sp.*, *Ricinus communis*, *Helianthus annus*, *Gossypium sp. Arachis sp.* These crops are used in certain preferred embodiments because they better facilitate the sequestration of metals and ions.

[0040] In certain embodiments of the present invention, the method of producing the agropolymers disclosed herein begins with the plant material (such as the seed coat, seed cover, hull, or husk) being powdered. In preferred embodiments, the powdering of the plant material is effected by a grinder. The plant material is subsequently micronized, which is accomplished by using a micronizer to obtain desired particle size (to be measured in microns).

[0041] The micronized plant material then undergoes either alkali treatment, hydrogen peroxide treatment, or a combination alkaline hydrogen peroxide treatment. In certain preferred embodiments, the alkali treatment is effected with sodium hydroxide, potassium hydroxide, sodium carbonate, or the like. In typical embodiments, the alkali solutions used to treat the

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micronized plant material have concentrations of alkali material in water of from about 1% by weight to about 10% by weight.

[0042] In other embodiments, the micronized plant material samples undergo hydrogen peroxide treatment either in combination with the alkali treatment or alone (without an alkali solution). In these embodiments, hydrogen peroxide is typically employed at a concentration of from about 5% by weight to about 30% by weight.

[0043] In embodiments where the combination alkaline hydrogen peroxide treatment is employed, the alkaline treatment may be performed either before hydrogen peroxide treatment, along with hydrogen peroxide treatment, or after hydrogen peroxide treatment. In certain preferred embodiments, the plant material undergoes the alkaline treatment and the hydrogen peroxide treatment simultaneously.

[0044] The above described treatments (including alkali treatment, hydrogen peroxide treatment, or combination alkaline hydrogen peroxide treatment) serve to create the property of enhanced metal or ion sequestration for the resultant agropolymer molecules.

[0045] After either alkaline treatment, hydrogen peroxide treatment, or a combination alkaline hydrogen peroxide treatment, the treated plant material is washed repeatedly with water or an acid solution to remove any alkaline and/or hydrogen peroxide residue. The acid solutions typically used in this step include solutions of diluted H<sub>2</sub>SO<sub>4</sub>, HCl, or HNO<sub>3</sub>.

[0046] The treated plant material is further contacted with an acid solution to remove any bound metals. If bound metals are present in the agropolymer material, such metal ions are

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eluted with acid solutions (typically of H<sub>2</sub>SO<sub>4</sub>, HCl, or HNO<sub>3</sub>) having concentrations of acid in water of from about 1% by weight to about 3% by weight.

The resulting agropolymer molecules are subsequently neutralized (to remove any remaining acid) through water washings or by the addition of a diluted alkali solution. The diluted alkali solution is typically a solution of about 1.0 M sodium hydroxide or potassium hydroxide.

[0048] Lastly, the resultant agropolymer molecules are removed from the supernatant through decantation and are dried to remove the remaining moisture content. This drying takes place either at room temperature or with the aid of a dryer at a temperature of from about 70 °C to about 80 °C.

The yield of agropolymer depends on the source of the plant material, the size of the plant material before treatment, and the reaction procedure or treatment adopted. Generally, yields of about 30 to 40% of the agropolymer were obtained when producing smaller agropolymer samples. Conversely, yields of about 75 to 80% of the agropolymer were obtained when producing larger agropolymer samples (for example, agropolymer samples larger than 150 microns). General analysis of the agropolymer yields show that the smaller agropolymer molecules are better able to sequester metals and/or ions.

[0050] In certain embodiments, the alkaline treatment without hydrogen peroxide is employed for producing agropolymers from cereals and millets. The micronized seed coats or hulls are first mixed with an alkaline solution (such as sodium hydroxide or potassium hydroxide). This alkaline treatment may be carried out either by the addition of an alkaline

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solution to the micronized seed coat or hull powder or by direct addition of alkaline powder or flakes to the micronized seed coat or hull powder followed by addition of water.

In embodiments involving alkaline treatment, the treated plant material releases a dark brownish-yellow substance. In these embodiments, the use of lower percentages of alkali (for example amounts of from about 5% to about 7.5%) requires more time to remove the dark brownish-yellow substance from the seed coats or hulls. However, the use of higher percentages of alkali (for example solutions of from about 20% to about 25% alkali) removes the dark brownish-yellow substance within about 3-4 hours.

[0052] Agropolymers developed according to the present invention have extensive industrial applications. They can be used effectively for pollution control in order to protect water and aqueous solutions in the environment from metal or ion contamination. In preferred embodiments, metals such as iron, copper, aluminum, arsenic, mercury, lead, and zinc as well as various ions may be removed from water and other aqueous solutions using the agropolymer disclosed herein.

In the present method, contaminated or polluted aqueous solutions (including metal-polluted or ion-polluted drinking water and ground water) are treated with agropolymers and/or metal-impregnated agropolymers. First, the polluted water is contacted with the agropolymers and/or the metal-impregnated agropolymers using a column or batch mode. This effects the ion or metal sequestration, thereby resulting in pollution-free water. The sequestration is typically carried out under optimum conditions wherein factors such as pH are closely regulated for maximum sequestration efficiency. In preferred embodiments, the

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agropolymers disclosed herein are capable of removing metals or ions from water or other aqueous solutions at the parts per million (PPM) to parts per billion (PPB) level.

[0054] Possible sites for the use of the agropolymers disclosed herein include areas where ground water is contaminated by toxic metals. For example, in certain embodiments, natural ground water, which is rich in arsenic, may be treated with the agropolymers of the present invention, and the arsenic content is significantly reduced so that the previously arsenic-rich water becomes potable water.

[0055] The following examples are intended to illustrate the invention and should not be construed as limiting the invention in any way.

#### **Examples**

### **Example 1: IR Spectroscopy Results of Various Agropolymers**

In these examples, raw husks, hulls or seed coats were micronized, and IR spectroscopy was performed using KBr pellets. The agropolymer samples used herein were treated with ferric chloride and dried before the IR spectroscopy was performed. IR spectroscopy of each sample was performed in three patterns: (A) total scans, representing 4000 to 500 wavenumbers (cm<sup>-1</sup>); (B) scans from 4000 to 2200 wavenumbers (cm<sup>-1</sup>); and (C) scans from 2000 to 600 wavenumbers (cm<sup>-1</sup>). Thus, in FIGURES 1-24, each figure is denoted (A), (B), or (C), and this denotation represents the IR spectroscopy pattern from the list above that was performed in the particular example.

[0057] As shown in FIGURES 1-4, IR spectra of various samples of rice husk revealed that the alkaline hydrogen peroxide treatment to rice husk resulted in more reactive bonds or more organometallic bonds.

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[0058] As shown in FIGURES 5-8, the IR spectra revealed more reactive organometallic bonds when samples of the *Setaria italica* husk were treated with iron.

[0059] FIGURES 9 and 10 reveal that alkaline hydrogen peroxide treated wheat (*Triticum sp.*) husk resulted in many organometallic bonds, particularly at  $2360 \pm 10$  and  $2340 \pm 10$  wavenumbers (cm<sup>-1</sup>).

[0060] The IR spectra of FIGURES 11 and 12 reveal that organometallic bonds were more predominant for *Panicum miliaceum* husk samples from 1600 to 600 wavenumbers (cm<sup>-1</sup>).

[0061] As shown in the IR spectra in FIGURES 13 and 14, alkaline hydrogen peroxide treated cotton seed (*Gossypium sp.*) hulls resulted in many organometallic bonds, particularly at  $2360 \pm 10$  and  $2340 \pm 10$  wavenumbers (cm<sup>-1</sup>).

[0062] As shown in the IR spectra of FIGURES 15 and 16, alkaline hydrogen peroxide treated castor seed coats (*Ricinus communis*) resulted in many organometallic bonds.

[0063] As shown in the IR spectra of FIGURES 17 and 18, alkaline hydrogen peroxide treated sunflower seed coats (*Helianthus annus*) resulted in many organometallic bonds.

[0064] As shown in IR spectra of FIGURES 19 and 20, alkaline hydrogen peroxide treated redgram seed coats (*Cajanus cajan*) resulted in many organometallic bonds.

[0065] As shown in the IR spectra of FIGURES 21 and 22, alkaline hydrogen peroxide treated greengram ( $Vigna\ radiata$ ) seed coats resulted in many organometallic bonds, particularly at  $2360 \pm 10$  and  $2340 \pm 10$  wavenumbers (cm<sup>-1</sup>).

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[0066] As shown in the IR spectra of FIGURES 23 and 24, alkaline hydrogen peroxide treated blackgram (*Vigna mungo*) seed coats resulted in many organometallic bonds.

[0067] Generally, the IR spectra compiled and described above show the capability of organometallic bonding held by agropolymers formed from various agricultural crops according to the present invention.

## Example 2: Examination of Metal Sequestration of Agropolymers Derived from Seed Coats or Hulls of Oryza Sativa, Panicum Miliaceum, and Setaria Italica

[0068] In this example, two 1.0 gram agropolymer samples were placed in 1000 mL volumetric flasks, which were filled to 1000 mL with 20.0 PPM standard copper and silver solutions respectively. These agropolymer samples were produced using the alkaline treatment method. The solutions were then kept for 2 hours with regular shaking in between, and were subsequently filtered. The resulting copper and silver present in the solutions was then estimated spectrophotometrically. The difference between the metal content present in solution before and after addition of agropolymer indicates the metal absorbing or sequestering capability of the particular agropolymer used.

[0069] Table 1 depicts the results of sequestered copper and silver by agropolymers.

TABLE 1
METAL SEQUESTRATION OF AGROPOLYMERS PRODUCED
BY ALKALINE TREATMENT METHOD

Sample	AGROPOLYMER	COPPER CONTENT	SILVER CONTENT
No.	PRODUCED FROM SEED	(MILLIGRAMS)	(MILLIGRAMS)
	COATS OR HULLS OF:	SEQUESTERED BY 1.0	SEQUESTERED BY
		GRAM AGROPOLYMER	1.0 GRAM
		SAMPLE	AGROPOLYMER
			SAMPLE
1.	Setaria italica	6.0	4.1
		-	

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2.	Panicum miliaceum	1.6	2.5
3.	Oryza sativa	4.5	4.7

[0070] As seen above, a 1.0 gram sample of the *Setaria italica* agropolymer absorbed or sequestered 6.0 and 4.1 milligrams of copper and silver respectively. Also, a 1.0 gram sample of *Panicum miliaceum* agropolymer sequestered 1.6 and 2.5 milligrams of copper and silver respectively. A 1.0 gram sample of the *Oryza sativa* agropolymer sequestered 4.5 and 4.7 milligrams of copper and silver respectively.

### Example 3: Examination of Metal Sequestration Using Metal-Impregnated Agropolymers

[0071] Agropolymers exhibit a higher capability of metal sequestration in solutions containing higher metal concentrations. Thus, further studies were performed in order to allow the agropolymers to absorb more metal in higher metal concentration solutions with longer retention times of up to 12 to 24 hours. Agropolymers were added to solutions containing metals such as iron or aluminum, and unbound metal was removed by thorough washings with water and/or by neutralization with alkali in cases where the reaction medium had an acidic pH. Subsequently, the material was dried. Metal-impregnated agropolymer was then placed in a beaker, wherein 250 mL of water was added and stirred well. Then, the agropolymer material was filled on a column mode. The agropolymer material present in the column was washed with 50 mL of 1.0 M acid to obtain bound metal. The metal content in acid washings was estimated spectrophotometrically. Table 2, shown below, depicts the amount of the metal content bound on the agropolymers.

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TABLE 2
BOUND METAL CONTENT PRESENT IN METAL-IMPREGNATED
AGROPOLYMERS PRODUCED BY ALKALINE TREATMENT METHOD

Sample	AGROPOLYMER PRODUCED FROM SEED	METAL CONTENT
No.	COATS OR HULLS + METAL	(MILLIGRAMS)
		SEQUESTERED BY 1.0
		GRAM AGROPOLYMER
		SAMPLE
1.	Setaria italica + ALUMINUM CHLORIDE	14.4
2.	Oryza sativa + ALUMINUM SULFATE	8.6
3.	Setaria italica + FERRIC CHLORIDE	4.7

[0072] As seen above, a 1.0 gram sample of *Setaria italica* agropolymer impregnated with aluminum chloride absorbed an amount of 14.4 milligrams of aluminum. A 1.0 gram sample of *Oryza sativa* agropolymer impregnated with aluminum sulfate absorbed an amount of 8.6 milligrams of aluminum. A 1.0 gram of *Setaria italica* agropolymer impregnated with ferric chloride absorbed an amount of 4.7 milligrams of iron.

## **Example 4: Examination of Arsenic Sequestration Using Agropolymers**

In this example, agropolymers bound with copper, zinc, and iron were used separately in determining the arsenic sequestering nature of such metal-impregnated agropolymers. 1.0 gram samples of agropolymer were added to 100 mL solutions containing 6.6 PPM sodium arsenate. The solutions were stirred well for a period of 3 to 4 hours. The arsenic content present in the supernatant was estimated spectrophotometrically. As shown below in Table 3, the metal-impregnated agropolymers successfully absorbed significant amounts of arsenic from aqueous solutions. The copper, iron, and zinc-impregnated *Setaria italica* 

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agropolymers absorbed from about 73 to about 75 percent of the arsenic present in solutions whose initial arsenic contents were 6.6 PPM.

TABLE 3
ARSENIC SEQUESTRATION OF METAL-IMPREGNATED AGROPOLYMERS
PRODUCED BY ALKALINE TREATMENT METHOD

Sample	AGROPOLYMER	INITIAL ARSENIC	ARSENIC
No.	PRODUCED FROM SEED	CONTENT (PPM)	SEQUESTERED BY
	COATS OR HULLS +		1.0 GRAM
	METAL		AGROPOLYMER
			SAMPLE
			(PERCENTAGE)
1.	Setaria italica + COPPER SULFATE (IMPREGNATED)	6.6	73.18
2.	Setaria italica + FERRIC CHLORIDE (IMPREGNATED)	6.6	73.3
3.	Setaria italica + ZINC CHLORIDE (IMPREGNATED)	6.6	75

[0074] Further studies showed that agropolymers without metal impregnation were also successful at absorbing arsenic. As shown in Table 4, agropolymers significantly reduced the arsenic content of natural waters containing arsenic. The samples of natural waters containing arsenic used herein were collected in West Bengal State in India.

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TABLE 4
ARSENIC SEQUESTRATION OF AGROPOLYMERS IN
NATURAL WATERS CONTAINING ARSENIC

Sample	AGROPOLYMER	INITIAL ARSENIC	ARSENIC CONTENT
No.	PRODUCED FROM SEED	CONTENT	PRESENT IN NATURAL
	COATS OR HULLS	PRESENT IN	WATERS AFTER
		NATURAL	TREATMENT WITH
		WATERS	AGROPOLYMERS FOR
			12 HOURS
1.	Setaria italica	325 PPB	40 PPB
2.	Oryza sativa	325 PPB	50 PPB
2.	Or yzu sunva	323111	

#### **Example 5: Examination of Fluoride Sequestration Using Agropolymers**

[0075] In this example, it was observed that agropolymers cannot absorb fluoride ion except when the agropolymer is bound with metals such as aluminum. Agropolymers bound with aluminum sulfate were added to a solution containing 5 PPM sodium fluoride. Specifically, 1000 milligrams of metal-impregnated agropolymer were added to 50 mL of a 5 PPM sodium fluoride solution. Two metal-impregnated agropolymer samples absorbed fluoride ion in amounts of 77.4% and 90.87 % respectively.

These metal-impregnated agropolymer samples were also able to remove fluoride ion from natural water samples containing fluoride. When a natural water samples having 4.15 PPM fluoride content were mixed with an aluminum chloride-impregnated *Setaria Italica* agropolymer sample and an aluminum sulfate-impregnated *Oryza Sativa* agropolymer sample respectively, in the amount of 1.0 gram agropolymer sample per liter of water, significant fluoride ion removal was observed.

# **Example 6: Examination of the Effects of pH Levels on Metal Sequestration of Agropolymers**

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In this example, the parameters for best metal sequestration and bound metal elution were studied. The effectiveness of the agropolymers disclosed herein is dependent upon pH levels suitable for metal sequestration. Typically, metals bound to the agropolymers disclosed herein can be eluted with mineral acids including sulfuric acid, nitric acid, or hydrochloric acid at pH levels of from about 0.8 to about 1.0. Furthermore, the agropolymer materials typically have maximum metal or ion sequestering capabilities at neutral pH ranges for most of the metals tested.

#### **Example 7: Examination of Iron Sequestration Using Agropolymers**

In this example, ferric chloride solution was passed through 1.0 gram samples of various agropolymers in a column at a flow rate of 2 mL per minute. The agropolymers had been treated using the alkaline hydrogen peroxide treatment, and bound metal content was estimated by eluting the bound metal with solutions of about 2% to 5% hydrochloric acid. Before elution, the unbound excess metal from the column was removed by washing with 2.5 pH hydrochloric acid solution. The bound metal content was estimated spectrophotometrically using par reagent at a wavelength of 535 nm.

[0079] Table 5 depicts the iron sequestration of agropolymers derived from *Oryza sativa*, Panicum miliaceum, Setaria italica, Cajanus cajan, Vigna mungo, Vigna radiata, Triticum sp., Ricinus communis, Helianthus annus, Gossypium sp., and Arachis sp.

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TABLE 5
IRON SEQUESTRATION OF AGROPOLYMERS PRODUCED
BY ALKALINE HYDROGEN PEROXIDE TREATMENT METHOD

Sample	AGROPOLYMER PRODUCED FROM SEED	IRON CONTENT
No.	COATS OR HULLS OF:	(MILLIGRAMS)
		SEQUESTERED BY 1.0 GRAM
		AGROPOLYMER SAMPLE
1.	Oryza sativa	5.15
2.	Panicum miliaceum	3.125
3.	Setaria italica	5.0
4.	Cajanus cajan	11.75
5.	Vigna mungo	6.875
6.	Vigna radiata	17.18
7.	Triticum sp.	3.125
8.	Ricinus communis	2.3
9.	Helianthus annus	11.25
10.	Gossypium sp.	6.25
11.	Arachis sp. (Red seed coat or cover of groundnut)	20.56

[0080] Generally, the results of the above examples illustrate the usefulness and effectiveness of agropolymers and metal-impregnated agropolymers in affinity columns, or the like, to purify aqueous solutions by binding, removing, sequestering, or reacting with reactive metals and ions. Thus, the agropolymer materials may be useful in various industrial applications including, but not limited to, the reduction of ground water contamination by industrial waste water, the improvement of affinity chromatography systems, and possibly even the manufacture of various agropolymer derivatives (such as biodegradable plastics, resins, or carrier materials).

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